# FIELD MEASUREMENT OF EFFECTIVENESS: HISTORICAL REVIEW AND EXAMINATION OF ANALYTICAL METHODS

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#### ABSTRACT

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Data are provided on 106 separate offshore experimental spills to determine dispersant field effectiveness. Effectiveness ratings for 25 of these spills were assigned by the experimenters; they vary from 0 to 100% and have an average of 33%.

Measurement techniques used for these experiments are reviewed and described. The techniques include: subsurface measurements to determine oil in the water column, surface sampling to determine oil remaining, dispersant application amount or distribution, and the use of remote sensing to visually observe the results or to quantify the area of surface oil. Existing means of detection and quantification appear to be effective.

Most experimenters have used subsurface oil data in an attempt to establish a mass balance and thereby an effectiveness value. This technique is critically examined using values from historical trials, and it is shown that the subsurface oil does not have a regular distribution in relation to the surface slick. Correlation cannot be established between concentrations at depth or with time and distance. This lack of correlation implies that mass balance values based on subsurface oil concentrations in relation to the

surface slick are not reliable. Effectiveness results claimed in the literature are also suspect because they do not correlate well with the maximum oil concentration seen at a given depth.

The mathematical relationships used to provide the integrated amount of oil in the water column are also examined. It is shown by simulation that effectiveness claimed is highly sensitive to both assumptions and mathematical treatment. Historical data are used to show that effectiveness values can vary over an order of magnitude depending on the algorithm used. Values in the literature are generally the highest one would obtain using reasonable algorithms.

A number of phenomena have been observed at spill sites. Herding of oil occurs immediately after dispersant application and has sometimes been misinterpreted as dispersion.

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Examinations of spills where slicks were monitored for longer than 3 hours show that extensive resurfacing of oil occurred. Resurfacing is particularly problematic because, depending on current and wind, resurfacing may occur outside slick boundaries. When this occurs, resurfaced oil is not included in subsequent calculations and consequently effectiveness is overestimated.

Field effectiveness cannot be reliably determined by using only measurements of oil in the water column. The distribution of oil in the water column is not known nor does it necessarily bear a relationship to surface slick boundaries. Furthermore, in the initial hours - perhaps as many as 7 - the oil concentration in the water column may be transitory as significant amounts of oil resurface. Remote sensing over a long term such as two or three days is suggested as the primary technique for monitoring experimental spills and for attempting to establish a mass balance.

Over the past 11 years, 106 spills have been laid out deliberately to test the effectiveness of oil spill dispersants. $^{1-20}$  These spills are summarized in Table 1. They do not include spills smaller than 0.2 m $^3$  (1 barrel). Many more of these types have been conducted than of the larger scale experiments, but have not been well documented in many cases. $^{18}$ ,21-25

The purpose behind most large scale experiments has been to document the effectiveness of oil spill dispersants in the field. The specific motive was to establish an effectiveness value or the percentage of the oil removed, attributed to the application of chemical dispersants versus that of slicks acted on by natural processes alone. Of the 106 slicks documented, 23 are controls used to establish a comparison. Percentage effectiveness is reported in 25 spills, and the average for these values is 33%. Values range from 2% to 100%. Most authors have not assigned effectiveness values because, as will be demonstrated later in this paper, effectiveness values are difficult to establish and variances are high. All values reported were made on the basis of water column oil measurements followed by attempts to obtain mass balance based on distance estimations and distribution extrapolation between measured points.

Additional points of interest are that 34 of these spills were conducted in French waters, 24 in American, 17 in Canadian, 17 in Norwegian, 9 in Dutch, and 5 in British waters. As a percentage of treatment methodologies, 37% were performed by ship spray systems, 32% by fixed wing aircraft, 22% by helicopter, and 8% were premixed with dispersants.

TABLE 1 -- Data from dispersant effectiveness trials

Location/ Identifier	Reference	Year	Number	Oil Type	Spill Amount (m <sup>3</sup> )	Dispersant	Application Method	Dose Rate D:0	Sea State	Claimed Effectivenes: (%)
North Sea	Cormack and Nichols (1,2)	1976		Ekofisk	0.5	10% Conc.	Snip, WSL	ŧ	<del>)</del>	ŧ
			2	Kuwait	•	10% Conc.	Ship, WSL	1:20	2-3	3
Wallops Island	McAuliffe et al (1,3)	1978	ო	Murban	1.7	Corexit 9527	Helicopter	7:5		1
			4	La Rosa	1.7	Corexit 9527	Helicopter	1:5		,
			ഹ	Murban	1.7	Corexit 9527	Helicopter	poort poort + + poort	<del>,</del> t	100
			9	La Rosa	1.7	Corexit 9527	Helicopter	) 	<b>,</b> 4	90
South California	Smith et al (4)	1978	-	North Slope	1.7	Control later Corexit 9527	Control then Helicopter	× 1:5	0-1	ı
			ω	North Slope	3.2	Corexit 9527	Airplane, Cessna	×1:5	<b>1</b> -0	ŧ
			on .	North Slope	1.7	Recovery + Corexit 9527	Helicopter	<b>√</b>	-J	ŧ
			10	Morth Slope	8.0	BP1100WD	Ship, WSL	>1:5	0-1	ì
				North Slope	8.0	Corexit 9527	Ship	>1:5	0-1	1

TABLE 1 (.../continued)

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Location/ Identifier	Reference	Year	Number	Oil Type	Spill Amount (m <sup>3</sup> )	Dispersant	Application Method	Dose Rate D:0	Sea	Claimed Effectiveness (%)
South California	Smith et al (4)	1978	12	North Slope	3.2	Corexit 9527	Airplane, Cessna	>1:5	1-2	i
			13	North Slope	8.0	Corexit 9527	Ship	>1:5	1-2	1
			14	North Slope	8.0	8P1100WD	Snip, WSL	×1:5	1-2	1
			15	North Slope	9.0	Several, Demonstration	Several, Demonstration	ı UO	1-2	i
Victoria	Green et al (1,6)	1978	16	North Slope	0.2	10%, 9527	Ship, WSL	4 * *	7	•
			17	North Slope	. 0.4	10%, 9527	Smip, WSL		gundê	•
			18	North Slope	0.2	10%, 9527	Ship, WSL	pund 6 8 pund	pare \$	í
Long Beach	McAuliffe et al (1,5)	1979	19	Prudhoe Bay	1.6	Control	Control	ţ	2-3	0.5
			20	Prudhoe Bay	1.6	2% Conc.	Snip	79:1	2-3	<b>x</b>
			21	Prudhoe Bay	. 1.6	2% Conc.	Ship	1:67	2-3	ഹ
			22	Prudhoe Bay	3.2	Conc.	Airplane, DC-4	1:20	2-3	78

TABLE 1 (.../continued)

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Location/ Identifier	Reference	Year	Number	0il Type	Spill Amount (m <sup>3</sup> )	Dispersant	Application Method	Dose Rate D:0	Sea	Claimed Effectivenes (%)
Long Beach	McAuliffe et al (1,5)	1979	23	Prudhoe Bay	1.6	Conc.	Airplane, DC-4	1:25	2-3	45
			24	Prudhoe Bay	1.6	Control	Control	•	2-3	П
			52	Prudhoe Bay	3.2	Conc.	Airplane, DC-4	1:27	2-3	09
			26	Prudhoe Bay	1.6	58	Ship	**************************************	2-3	uma uma
			27	Prudhoe Bay	1.6	5%	Ship		2-3	29
Mediterranean, Protecmar I	Bocard et al (7)	1979	28-41	Light Fuel	3 each	BP1100X BP1100WD Finasol OSR-5 Corexit 9527	Ship, Helicopter, various and Airplane CL215	ŧ	<b>(*)</b>	t .
Mediterranean, Protecmar II		1980	42-49	Light Fuel	1-5.5	z	3	ı	1-3	ł
Mediterranean, Protecmar III	Bocard and Gatellier (1,7,8)	1981	20	Light fuel	6.5	Dispolene 325	Airplane, CL215	~	1-2	90
		•	ď	Light Fuel	6.5	Shell	Airplane, CL215	1:3	2-3	ŧ
			25	Light Fuel	6.5	Control	Control	f	1-2	ı
Newfoundland	Gill et al (9)	1981	53	ASMB	2.5	Control	Control			ŧ
			54	ASMB	2.5	Corexit 9527	Airplane, DC-6	21.	, <b>4</b>	i

TABLE 1 (.../continued)

Location/ Identifier	Reference	Year	Number	011 Type	Spill Amount (m <sup>3</sup> )	Dispersant	Application Method	Dose Rate D:0	Sea State	Claimed Effectivenes (%)
Norway	Lichtenthaler and Daling (1,10)	1982	55	Statfjord	0.2	Control	Control	ı	2-3	9.0
			95	Statfjord	0.2	10% Conc.	Ship	2::	2-3	9
			27	Statfjord	0.2	10% Conc.	Ship	1:10	2-3	7
			28	Statfjord	0.2	Control	Control	ı	2-3	5.6
			65	Statfjord	0.2	10% Conc.	Ship	1:17	2-3	19
			09	Statfjord	0.2	10% Conc.	Ship	1:18	2-3	22
			61	Statfjord	0.2	10% Conc.	Ship	1:13	2-3	2
North Sea	Cormack (1,11) 1982	1982	62	Arabian	20	Control	Control	ı	<b>,4</b>	•
			63	Arabian	20	Corexit 9527	Airplane, Islander	1:2	, week	ŧ
			64	Arabian	20	Corexit 9527	Airplane, Islander	1:4	-	•
Mediterranean Protecmar V	Bocard et al (1,12)	1982	99	Light Fuel	m	10% Díspolene 325	Ship	1:2	က	ı
			99	Light Fuel	S	Dispolene 325	Airplane, CL215	1:2.4	m	ı

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TABLE 1 (.../continued)

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Location/ Identifier	Reference	Year	Number	Oil Type	Spill Amount (m <sup>3</sup> )	Dispersant	Application Method	Dose Sea Rate State D:0	Claimed Effectivenes (%)
Protecmar V	Bocard et al (1,12)	1982	19	Light Fuel	5	Dispolene 325	Ship	1:2.8 2	•
			89	Light Fuel	2	Dispolene 325	Airplane, CL215	1:2.8 2	•
			69	Light Fuel	3.5	Dispolene 325	Ship	1:2.6 1-2	•
			70	Light Fuel	4	Dispolene 325	Helicopter	1:2.9 1-2	ı
			7.1	Light Fuel	2	Premixed	Premixed	1:20 1-2	40-50
			72	Light Fuel	S	Control	Control	- 2	•
Molland	Delvigne (1,13)	1983	73	Statfjord	7	Control	Control	- 1-2	5
			74	Light Fuel	2	Control	Control	- 1-2	2
			75	Statfjord	2	Control	Control	1	2
			9/	Statfjord	2	Finasol OSR-5	Airplane	1:10-30	2
			11	Light Fuel	2	Finasol OSR-5	Airplane	1:10-30 1	2
			78	Statfjord	8	Finasol OSR-5	Premixed	1:20 2-3	36

TABLE 1 (.../continued)

Location/ Identifier	Reference	Year	Number	Oil Type	Spill Amount (m <sup>3</sup> )	Dispersant	Application Method	Dose Rate D:0	Sea State	Claimed Effectivene: (%)
Holland	Delvigne (1,13)	1983	79	Light Fuel	2	Control	Control	ţ	2-3	2
			80	Statfjord	2	Finasol OSR-5	Airplane	1:10-30 1-2	1-2	2
			81	Statfjord	2	Finasol USR-5	Airplane	1:10-30 1-2	1-2	2
kalifax	Swiss and Gill (1,14,15)	1983	88	ASMB	2.5	Corexit 9527	Helicopter	1:20	,4	2.5
			83	ASMB	2.5	Control	Control	ŧ	,4	<b>J</b>
			84	ASMB	2.5	Corexit 9550	Helicopter	3	<b>,4</b>	13
			85	ASMB	2.5	Control	Control	ı	pomě	
			98	ASMB	2.5	BP MA700	Helicopter	1:10	2-3	10-41
			87	ASMB	2.5	Control	Control	ŧ	2-3	7
Norway	Lichtenthaler and Daling (16)	1984	88	Statfjord	10	Control	Control	ŧ	<b>~</b>	ŧ
			68	Statfjord	10	Corexit 9527	Airplane, Islander	1:75	<b>,4</b>	i
			90	Statfjord	2	Control	Control	i	2	ı

TABLE 1 (.../continued)

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Location/ Identifier	Reference	Year	Number	0il Type	Spill Amount (m3)	Dispersant	Application Method	Nose Rate S	Sea State	Claimed Effectivene (%)
Norway	Lichtenthaler and Daling (16)	1984	16	Statfjord	10	Corexit 9527	Airplane	1:80	2	ı
			35	Statfjord	12	Corexit 9527	Premixed	:33	2	1
			93	Statfjord	10	Corexit 9527	Airplane	1:50	i	t
Brest, Protecmar VI	Bocard (7,17)	1985	94	Fuel Oil	S.	Control	Control	ı	<del>(</del>	ı
			95	Fuel Oil	28	Dispolene 355	Helicopter	1:9	ęq	ť
			96	Fuel Oil	part of above	Dispolene 355	Ship-spray	1:9		•
			97	Fuel Oil	part of above	Dispolene 355	Ship-aerosol	1:9		ŧ
Haltenbanken	Sørstrøm (19)	1985	86	Topped Statfjord Crude	12.5	Control	1	ı	1-2	
			66	Topped Statfjord Crude	12.5	Finasol	Premixed, Injected 3 m below surface	1:50	7-5	ı

Location/ Identifier	Reference	Year	Number	0il Type	Spill Amount (m <sup>3</sup> )	Dispersant	Application Method	Dose Rate D:0	Sea State	Clained Effectivene (%)
Haltenbanken	Sørstrøm (19)	1985	100	Topped Statfjord Crude	12.5	Control	ł	ı	1-2	•
			101	Topped Statfjord Crude	12.5	Alcopol (demulsifier)	Premixed 2	250 ppm	1-2	ŧ
Beaufort Sea	Swiss et al (20)	1986	101 (CA)	Topped Federated Crude	2.5	Control	ı	ŧ	1-2	•
			102 (CB)	Topped Federated Crude	2.5	Control	i	i	1-2	l ,
			103 (C1)	Topped Federated Crude	2.5	BP MA700	Helicopter	7:10	2-3	•
			104 (T1)	Topped Federated Crude	2.5	BP MA700	Helicopter	,4 4 * ,4	2-3	1
			105 (T2)	Topped Federated Crude	2.5	Corexit CRX-8	Helicopter	,t  t	2-3	ı
			106 (C)	Topped Federated Crude	2.5	Control	1	ŧ	2-3	ı

Abbreviations: ASMB - Alberta Sweet Mixed Blend; Conc. - Concentrate; WSL - Warren Springs Laboratory

Previous authors have analyzed field experiments, in lesser numbers, and have generally concluded that field tests show effectiveness problems with dispersants. 1,26 Others have noted the variety of analytical techniques used and the problems associated with conducting these field operations and obtaining data to determine the actual effectiveness. 7,27

# ANALYTICAL ASPECTS OF FIELD TRIALS

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Table 2 is a summary of the analytical means employed at the field trials summarized in Table 1. This table lists the means used to measure oil content in the water column, sampling the oil or dispersant on the water surface, and for remote sensing. Notably absent are techniques used for the measuring of dispersant in oil; reliable means still do not exist to measure the amount of dispersant in oil, especially in the case of field trials. This means that the actual loss of dispersant to water is not known, as well as the amount of dispersant retained in the oil, both on the surface and in the water.

Reviews of oil-in-water analytical techniques have been published. 29-31 In recent years, at field trials, most oil in the water column has been measured using fluorometers or turbidimeters. Both instruments possess the ability to measure the dynamic range of the encountered concentrations. 30,31 The accuracy of the measurements, in both cases, is dependent on the accuracy of calibration. Obtaining accurate calibration results is difficult since an instrument's response for a given amount of oil is sought and oil will largely cling to the walls of the calibration pipes and vessels or float to the surface. This can be partially alleviated by adding dispersants or other surfactants, although in the author's laboratory it was found that a maximum of 70% of the oil in the range of 1 to 30 ppm was actually in the water, even with large amounts of

TABLE 2 -- Monitoring methods used at dispersant field trials

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4 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6	-		Water Sampling	ling	Surface Sampling	poling		Remote Sensing	g <b>r</b> i
Control of the Contro	Location	Wet hodol ogy	Depths (m)	Analysis	Method	Use	Dispersant		
Corneck and	Britain	Knudsen bottles	2-15		4		the contract of the contract o	S. IOSCIECT	š
			<b>;</b> !	ייים בארביים		mater content, emulsification	Krowe-cote cards	•	•
	. New Jersey	pumping to bottles	1,3,6,9	¥	,	t	ı	7	,
et al 161	Canada	pumping to	1,3.5		•			photographs	OCCUPANT AT
왕 : #		Tluorometer and to bottles, towed fluorometer		131300 COS		s	ì	photo	document at
	U.S.A. - Long Beach	pumping to bottles	1,3,6,9	IR, GC	,	ŧ	1	•	
	****	pumping to bottles	ب ب ب	Ş			1	photographs	document at
ong Mg w Mg d	· Lony Brack			<b>*</b>		,	sued	Color photographs	document at
Bocard and	france - Toulon	pumping to bottles			•			and vides	
7	(Protecuar 183)	and instrument	2.5	- IN (bottles) - turbidimeter (direct)	Sorbent	í	í	æ	Slick area
Gill and Ross	Canada - St. John's	pumping to fluorwaster and bottles	1,2,4	bottles not done - spoiled	sorbent	thickness	Krome-cote cards	* *	slick area surface
									tension
								laser fluorosensor	document at
Lichtenthaler and Daling [10]	NOTES SEE	Sample Dottle	1,2.5,5,9	ક	•	•		photo	
Comment of the contract of the	Britain Seritain	pumping to bottles	1,3,6,9	GC. fluorometer				ŧ	•
					sorbent	thickness	Krome-cote cards	and parts	COCHERNIA!
					sk immer	weathering			

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dispersant. Without dispersant this amount was as low as 10%, depending on the oil type. The effect on the final measurement, of this loss of oil, is to overestimate the oil during the actual measurement. Calibrations made in the author's laboratory and used with field fluorometric data resulted in overestimations by as much as an order-of-magnitude. Commonly, measurements in the field are double or triple the actual value. This is due to lack of compensation for oil loss during calibration. With this being the major source of error for fluorometric and turbidmetric measurements, results from these instruments tend to be high rather than low. Both instruments, especially the turbidimeter, however, have a tendency to provide useful measurements over a range of 2 orders-of-magnitude with respect to a given instrument range. Lower concentrations may not be accurate when instruments are calibrated at high levels. Turbidimeters, by nature of their construction, are not capable of measuring low quantities of oil in the water column.31

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Earlier field trials often used grab samples and subsequent gas chromatographic (GC) analysis to determine oil in water. These types of measurements tend to be low, as the greatest sources of errors are oil loss in the sample jar due to loss of the volatiles or adhesion to the walls.<sup>32</sup> These types of losses have been avoided by some investigators by putting a chlorinated extractant directly into the bottle before the water sample is added.<sup>7</sup>,<sup>14</sup> The difficulty in pumping samples to the surface, the questions of accuracy associated with this pumping, and the difficulties in handling sample bottles has diminished the use of this methodology in recent years.

Infrared (IR) analysis of oil in water has occasionally been used. It is believed to be as accurate as GC in the range of 0.05 to 20 ppm.<sup>29</sup>

One experimenter used a unique analytical scheme of tagging the oil with a radioactive tracer and subsequently counting the samples.<sup>33</sup> Results using this sophisticated methodology correlated very well with fluorometric data. It is interesting to note that the fluorometric data was 10% of the radioactive data, the same factor that the author noted previously in this paper, as a minimum loss for the calibration of a fluorometer.

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Several investigators have tried to determine the deposition rate of dispersant from aircraft sprays by catching the spray on Krome-cote cards or absorbent sheets. 1,9,11,13,14 The cards or sheets are then washed with a solvent and the amount of dispersant determined in the solvent. Since analytical methods of determining dispersants are not readily available, the dispersant is usually dyed to perform this experiment. The dye is an oil-soluble dye such as "Oil Red B" (used in North America to colour gasoline for tax purposes). With the addition of dye, the solvent washing of the Krome-cote cards can be analyzed directly by colorimetry. Few results have been published; however, deposition rates have ranged from 30 to 80%. The use of Krome-cote cards also enables the measurement of droplet size. Constant droplet spreading rate can be calibrated and used to directly read droplet size. Again, few results have been published because many cards have been spoiled by sea spray or subsequent handling. The same fate has applied to many sorbent pads in past field trials. In addition to sea spray, other problems with this technique have been noted, including the pitching and yawing of any device or craft holding the sorbent pad and the large unexplained lack of homogeneity in values from those cards or pads actually recovered.

Surface oil has been sampled by a number of investigators to determine the extent of weathering or slick thickness. 1,7,8,9,11,14,16,18 Methods

Analysis on these samples have generally included viscosity, density, or GC analysis to determine degree of weathering. Analysis of amount of water present has also been included. This is to estimate the extent of water-in-oil emulsification. Samplers have also been devised which can be calibrated to estimate slick thickness.<sup>34</sup> Results from this procedure are very scattered both as a result of the lack of homogeneity of the slick and because of difficulties in obtaining a "clean" sample.

Remote sensing has increasingly become the means to monitor dispersant field trials.35-38 Slicks can be monitored without the usual perils and limitations of surface craft. Remote sensing can provide a synoptic view of the entire slick, positional records and thickness profiles of the slicks. Photographs, which need little explanation, have been used at most field trials. Similarly, video recording is now coming into vogue and provides analogous capability. Infrared (IR) scanners have been used at many trials. IR imagery provides a thickness profile map of the slick.<sup>37</sup> The correlation of these profiles to slick thickness has been attempted. However, variances in which a particular signal level occurs is thought to depend on sun angle, air and water temperature, wind speed, and oil type. 37,39 A number of investigators have used the loss of IR imagery as an indication of the rate of disappearance of the thick slick, since IR only shows the thick slick (cutoff at 10 to 50 microns is estimated). A recent experiment in the Arctic, however, showed that the rate of disappearance of the IR image (thought to be equivalent to the thick slick) was faster or as fast in the three control slicks as in the three treated slicks.20 The reason for this particular phenomenon may be that the treated slicks formed "herdy balls" or "pea flock" in the thick oil area and these may have been

interpreted by the IR scanner as thick oil.<sup>20</sup> Generally, the IR image disappears after a few hours, more rapidly if the oil is dispersed. Another anomaly was also observed in this field trial when, after the disappearance of the IR image in the first few hours, the reappearance in IR imagery of the slick the next day.<sup>40</sup> Clearly, even this methodology is not completely understood, nor can one make definitive statements using IR imagery alone.

Ultraviolet (UV) imagery has been used frequently at spill tests. UV imagery offers a view of the entire slick down to very small thicknesses. The limit is suspected to be around 0.01 microns, or that of a mono-molecular layer of oil. 37 UV scanners have also been coupled with IR scanners to provide an overall map of the oil. UV imagery represents the sheen portion and IR imagery represents the thicker portions. 37 Anomalies for UV imagery include the detection of natural oils and phytoplankton as oil; however, false imaging is much less for UV than IR. 37

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Oil on the surface damps the micro-capillary waves and thus provides a means of detection by radar.<sup>37</sup> Radar has been used at a few spill trials; however it does not provide thickness information, and imagery is generally not as good as that for IR or UV. Furthermore, radar is susceptable to many false images resulting from phytoplankton, wind slick, freshwater slicks, and calm areas on the sea. The advantage of radar is its ability to detect slicks at long-range (from 40 to 100 kilometers (km) depending on the type of radar and altitude of the aircraft).<sup>37</sup> Its usefulness at dispersant field trials is questionable.

Microwave thickness measurements have been attempted at one field experiment, however the use was experimental and the results were inconclusive.  $^{41}$ 

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A review of the literature on field trials reveals an interesting feature, that is most experimenters were struck with an unusual occurrence or observation which occurred at their trial. Some of these have been further investigated and processes defined, others have not. Many of these occurrences interfere with the assessment and evaluation of the effectiveness of dispersants.

The most important phenomena discovered at field trials, and later described in detail in laboratory studies, is that of herding. 42,43,44

This is the movement of oil by the dispersant. The dispersant has a greater surface tension with water than the oil. When large droplets of dispersant break through the oil layer, the greater surface tension in that area enables the dispersant to push the oil aside until all the forces are balanced. This usually means that most of the spray swath is affected and the oil is pushed into narrow ribbons or pools within the area. The process is transitory. The dispersant is largely soluble in water and is carried away and the oil is allowed to re-spread over the area. The entire process generally takes 2 to 10 minutes. Workers at early field trials observed herding and felt that this was actually dispersion. In fact, workers have since discovered that when herding takes place, dispersion effectiveness is low, as most of the dispersant was lost to the water column. 42

Herding is thought to occur only when the applied droplets of dispersant are large enough to penetrate the oil layer. The size at which this occurs is not clear and was originally thought to be 500 microns, but recent investigations have shown that there may be other factors involved as well.<sup>44</sup> Herding clearly does not occur all the time even though

circumstances may be similar. Bocard has recently reported and documented an interesting phenomena observed during a field trial in France. Herding was observed to occur both upwind and downwind of a dispersant spray boat. Investigation of the phenomenon has failed to reveal any obvious cause of the herding upwind.

Herding is important from a remote sensing point-of-view. When herding occurs, a discontinuous area is seen. Since the herded ribbons and pools of oil are too small to be detected from the air, the oil appears to have suddenly disappeared. When the oil respreads, it again appears. This was observed and documented in the series of images of one oil spill dispersant trial. 35

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Resurfacing of dispersed oil has been observed in a number of trials. 7 Bocard has indicated that resurfacing is generally observed after three hours: however, evidence of resurfacing has appeared in the form of expanded sheen areas as early as 1.5 hours.<sup>33</sup> Resurfacing of dispersed oil would only be observed if one was monitoring the sea surface for several hours, and the dispersed plume from which the oil was surfacing is near the original slick. Long-term (e.g. up to 12 hours) remote sensing is generally required to show evidence of resurfacing. Those who have monitored in this manner suspect that much of the dispersed oil resurfaces. 7 It is questionable then, if this is the case, how effective a particular application is if the dispersed portion resurfaces and the phenomena is difficult to measure. Many field tests surveyed in this paper did not include remote sensing surveillance or other provision for measuring resurfacing nor did most field work last beyond three hours. Long-term (e.g. 24 or 48 hour) measurements may be necessary to take in the effect of resurfacing.

Another phenomenon observed at field trials is the formation of oil-emulsion-like objects in the thick portion of the slick. 45-47 These have alternatively been called "Pea Floc" and "Herdy Balls". The author observed these at the 1986 Beaufort Sea dispersant trials. The appearance of these is similar to a dried pea, however, they are brown and "mushy" looking. In the case of these above-mentioned trials, much of the area once occupied by the thick slick was covered by these objects.<sup>47</sup> Initial work at the Esso laboratory in Calgary has suggested that these may be a three-way oil-in-water-in-oil emulsion. 48 Such an emulsion has been found in the Esso laboratory. It requires an excess of dispersant (as high as 1:1) to form. This emulsion is unstable, also as observed at the field trials, and requires a mono-molecular layer of oil or dispersant to hold it into place; if not, rapid breakdown of this emulsion occurs. These objects, although few in number and apparently few in distribution, have been interpreted from the IR imagery as being thick oil. 20,38 This effect may have led to the result that the thick areas for all three control slicks appeared to disappear faster than the thick areas of the treated slicks.<sup>20</sup> This result, in itself, is rather unlikely since it would imply that dispersants had the reverse effect of that intended.

67.

60 11 22

Another phenomenon observed at field trials is the presence of "lace" or sheen areas where small circular areas of open water are evident. These areas are thought to be areas of sheen sprayed by dispersant. Explanation of the holes in the sheen is that they were caused by herding or that they represent oil lost by dispersing into the water column. The presence or formation of lace is not felt to be important to the measurement of effectiveness.

Discrepancies in observations and impressions between observers from surface vessels and aircraft are numerous. The last two phenomena noted are not observed from aircraft due to the small size scale. Observers on surface vessels often do not observe macro features, such as the formation and movement of the dispersed oil plume. In most field trials it has been recognized that resolution of observations from the surface and air is a task to be done before data can be properly interpreted.

# ATTEMPTS TO DETERMINE MASS BALANCE

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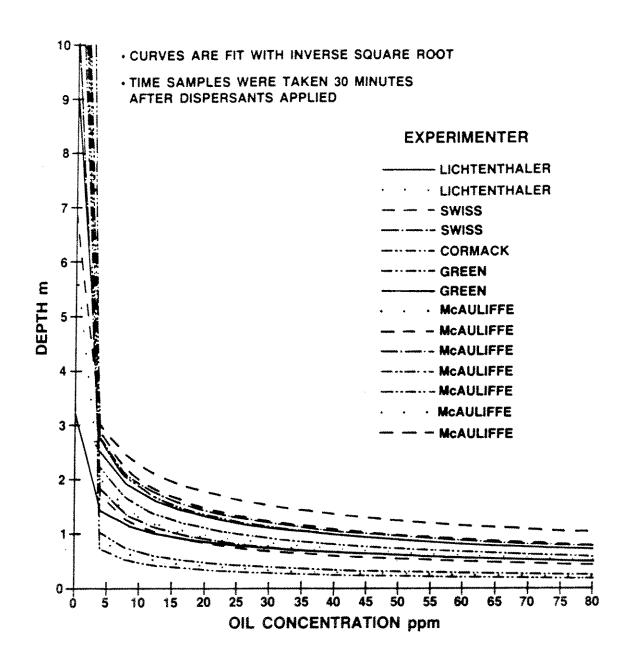
A number of workers have attempted to measure dispersant effectiveness by performing a mass balance of oil-in-water.<sup>3,5,33</sup> A number of assumptions are necessary to construct such a mass balance:

- 1. The distribution of oil in the water column has a known or measurable distribution, geometry or function.
- 2. The distribution of this oil in water can be measured with respect to the slick.
- 3. The oil-in-water-column measurements taken at different points in time are useful. Technology does not exist to measure a large number of oil-in-water concentrations in a synoptic fashion, although it has been attempted.<sup>49</sup>
- 4. Some water column oil concentration data can be used to form an entire picture of the oil concentrations beneath a slick using mathematical algorithms. Generally, this implies that one takes concentrations in a "block" and adds the various blocks together. Additionally, the implication is that averages are a good estimation of depth-concentration profiles.

The first assumption, that the oil has a known or measurable geometry in the water column, is difficult to establish. However, a geometry or distribution must be known before integration can be accomplished. 50 Brown and co-workers have performed a series of tests in a wave basin with fixed geometry of all discharges, sampling ports and cameras, and have noted two interesting results. 27 First, the shape and geometry of the underwater plume varied widely. Secondly, the direction(s) that the plume or, in some cases, plumes travelled also varied dramatically. No correlation to wind or induced current was established. This result implies that the geometry and movement of sub-surface plumes is poorly understood and integration of sub-surface concentration data is not valid mathematically.

Data analysis on numerical results in the literature from these trials did not reveal any uniform structure to oil concentration in the water column with respect to either time or space.

Sub-surface concentrations with depth at 30 minutes after dispersant application fit square root or log function equally well. A series of these are shown in Figure 1, along with the name of the primary author from whose paper the data was derived. The correlation coefficient for both curve fits ranged from 0.82 to 0.96 and were approximately equal over the 14 sets of data used. A number of other functions were attempted with a significantly poorer fit. It is important to note that only at 30 minutes after dispersion did these functions form such a unified set of curves, and also that the actual values of oil concentration varied over two orders-of-magnitude for a given depth. The presence of this correlation of depth and concentration is probably due to the similarity of process (dispersion here), whereas the lack of correlation after 30 minutes is that the process is oceanographic and



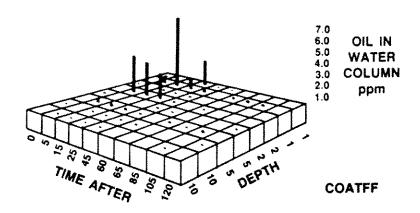
turbulence transport and is different in every case. Figure 2 shows the lack of correlation in concentration with depth versus time for the Canadian Offshore Aerial Applications Task Force (COAATF) experiment near Halifax. Similar correlations were performed with data from McAuliffe, Lichtenthaler and Bocard, all showing the lack of correlation.

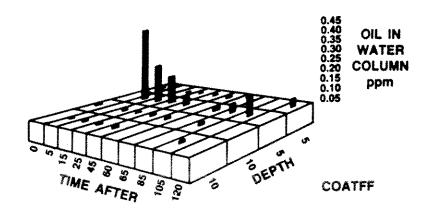
The second assumption is that the oil concentration can be measured with respect to an X, Y coordinate system, such as position below the slick. Since surface slick movement and sub-surface plume movement are not necessarily coupled and are due to different forces, such an assumption is not fully valid. As the oil originates from the surface slick, the plume will for some time pass under the slick depending on the differential velocity between slick and plume.

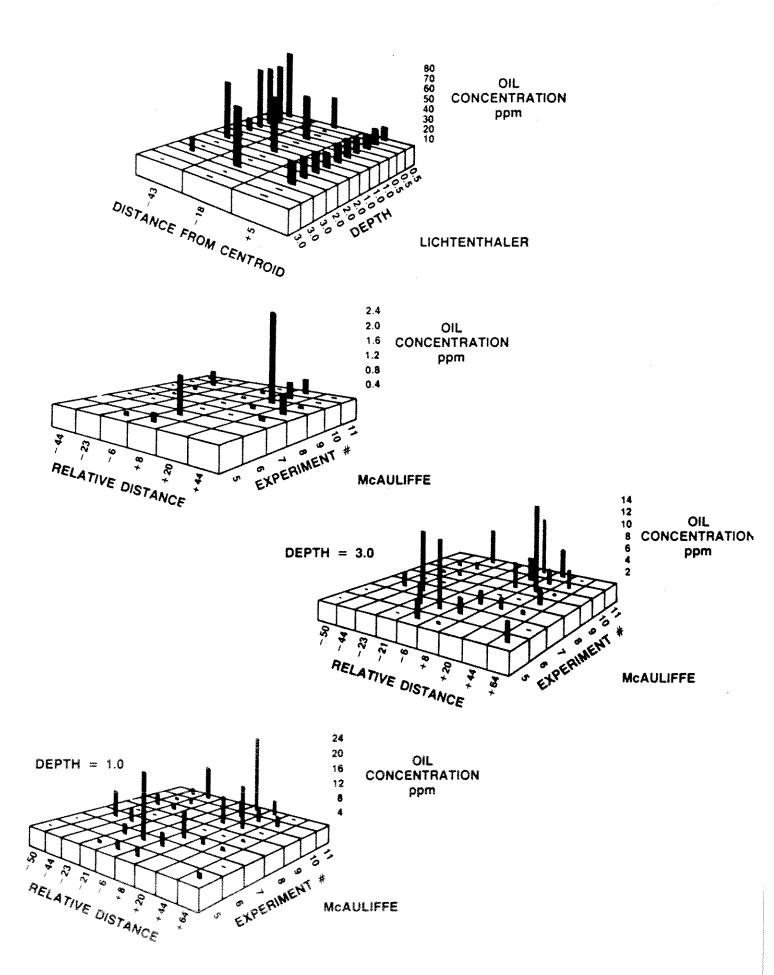
Figure 3 presents a correlation between concentration and distance along the windward axis of a slick. Figure 4 presents the same correlation, however, along the slick axis perpendicular to the wind. Distance in both figures refers to relative distance where 100 is on one edge, -100 another edge, and 0 the centre of the slick. The data are taken from McAuliffe and Lichtenthaler as noted. 5,10 In both cases, there is an obvious lack of correlation between concentration and the distance along a slick's axis, nor is there any apparent structure to the data.

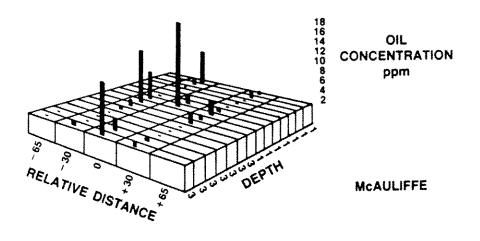
The third assumption, that data at various times can be used, has been dealt with above. It has been established that there is poor correlation between time and concentration.

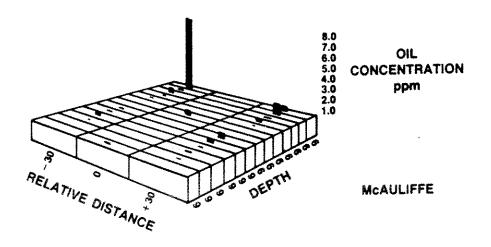
The fourth assumption made in attempting a mass balance is that an appropriate mathematical function can be found to relate sub-surface concentrations and dimensions to an overall measurement of oil in water. Two schemes to perform this are in the published literature. McAuliffe and











co-workers used the total of 4 layers beneath the slick.<sup>5</sup> The first layer was the body of water 0 to 2 metres (m) below the slick. The concentration taken was the average of all the 1 m depth concentrations. The second layer was the body of water 2 to 4 m below the slick. The average concentration was taken to be the average of all 3 m depth concentrations. The third layer is the 4 to 7.5 m layer and uses measurements at the 6 m depth. The fourth layer is from 7.5 to 10.5 m and uses the measurement from the 9 m depth of water. The volume of each layer is evaluated using the main slick length and 2/3 of the slick width.

The second scheme in the literature is that reported by Swiss and  $Gill.^{14},^{15}$  Four layers are also used: 0-1.5 m represented by the concentration at 1 m, 1.5-7.5 m represented by the concentration at 2 m, 3.5-7.5 m represented by the concentration at 5 m, and 7.5-12.5 m represented by the concentration at 10 m. The scheme is not remarkably different from that of McAuliffe's, which is noted above.

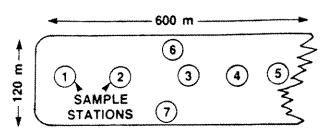
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Both schemes are compared in Figure 5. The data is that published by McAuliffe and co-workers for a slick laid during the 1979 South California trials.<sup>5</sup> In the paper the authors give a value of 45%. In applying the methodology from the same paper one gets essentially the same result (43%). These results are equivalent, since the exact value of background oil and roundoff errors will make the difference. Using the scheme proposed by Swiss and co-workers, a value of 41% is obtained. The difference is minimized because of the same area used as in the McAuliffe scheme. In the Swiss scheme, the actual area is used in practise rather than 2/3 of the width times the length. To illustrate further the variances caused by using different integration schemes, Figure 5 shows a scheme using all the areas

### **EXAMPLE SITUATION**

#### SLICK GEOMETRY

# SUBSURFACE CONCENTRATIONS (ppm)



DEPTH (m)		5	TATI	ON NO	<b>JMBE</b>	R_		AVE.
	1	2	3	4	5	6	7	
1	.58	1.62	4.87	3.76	3.09	.83	.17	2.13
3	.75	1.23	4.09	2.65	2.87	.82	.27	1.81
6	.33	1.0	.82	1.23	1.33	.60	.11	.77
9	.04	.44	.04	.49	.04	.38	.04	.21

TOP VIEW OF SLICK

OIL SPILLED = 1.6 m<sup>3</sup> (10 BARRELS)
OIL REMAINING AFTER EVAPORATION = 1.22 m<sup>3</sup>

ALL DATA ACTUAL VALUES FROM McAULIFFE 1981

# CALCULATION BY METHOD OF McAULIFFE

• VOLUME IN EACH LAYER = AVERAGE CONCENTRATION × ⅔ × CALCULATED AREA × DEPTH

• LAYER	DEPTH REPRESENTED (m)	MEASURED DEPTH (m)	OIL IN EACH LAYER (m3)
1	0 - 2	1	.20
2	2 - 4	3	.17
3	4 - 7.5	6	.12
4	7.5 - 10.5	9	.03
			TOTAL = .52 =>43% EFFECTIVENESS

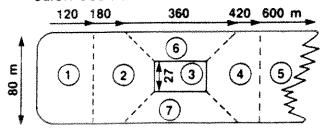
# CALCULATION BY METHOD OF SWISS

• VOLUME IN EACH LAYER = AVERAGE CONCENTRATION × ACTUAL AREA × DEPTH

• LAYER	DEPTH REPRESENTED (m)	MEASURED DEPTH (m)	OIL IN EACH LAYER (m3)	
1	0 - 1.5	1	.15	
2	1.5 - 3.5	2	.17	
3	3.5 - 7.5	5	.14	
4	7.5 - 12.5	10	<u>.04</u>	
	*USING SAME DATA AS ABOVE		TOTAL = .50 =>41% * EFFECTIVENESS	

# CALCULATION BY INTEGRATING EACH COMPARTMENT

SLICK SUBCOMPARTMENTS AND THEIR DIMENSIONS



\* USING SAME DEPTHS AND CRITERIA AS MCAULIFFE

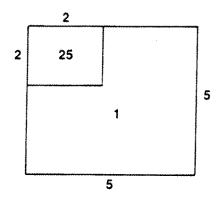
LAYER*	OIL IN EACH LAYER (m3)
1	.19
2	.16
3	.08
4	.02
	TOTAL = .45 => 37% EFFECTIVENESS

under the slick and integrating 28 compartments rather than just 4. This results in the value of 33% instead of the published 45% effectiveness result. Integrating each individual compartment will yield more accurate results than averaging values, given that the compartments are of different sizes and, secondly, that the values of concern are different. Figure 6 illustrates this basic mathematical concern. Average values will produce the same values as the sum of individual same-size compartments. However, when the compartments are of different sizes, the integral is very sensitive to method of treatment.

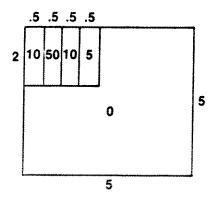
Some authors have given estimates of effectiveness based on maximum concentration achieved in the water column. S1 values using this assumption and other values are shown in Table 3. Effectiveness would vary a great deal depending on which scheme is chosen. Since concentrations of oil-in-water vary widely and appear to have little structure, use of maximum concentration estimates are not likely to be reliable. The correlation of maximum concentration of oil at the 1 m depth and the claimed dispersant effectiveness is shown for a number of field trials in Figure 7. The correlation is very poor indicating probably both a variety of approaches for the assessment of effectiveness and the lack of relationship between both.

#### SUMMARY AND CONCLUSIONS

A large number of dispersant field trials have been conducted worldwide. Methodologies and results from these vary significantly. Measurements of effectiveness at these trials were, in early years, attempted by integrating water column concentrations. This was based on the assumptions that a regular distribution of oil in the water column existed, that this was



SITUATION: VALUE OF 25 MEASURED IN SMALL AREA, 1 IN AREA AROUND



SITUATION: SIMILAR TO ABOVE BUT MEASUREMENTS MORE SITE SPECIFIC

### CALCULATIONS OF INTEGRAL

A. RELEVANT AREA ONLY

$$2 \times 2 \times 25 = 100$$

B. SUM BOTH AREAS

$$2 \times 2 \times 25 = 100$$
  
 $5 \times 5 \times 1 = 25$   
 $125$ 

C. AVERAGE VALUES

$$\frac{25 + 1}{2} = 13$$

$$5 \times 5 \times 13 = 325$$

D. SUM ONLY EXACT AREAS

$$.5 \times 2 \times 10 = 10$$
  
 $.5 \times 2 \times 50 = 50$ 

$$.5 \times 2 \times 10 = 10$$

$$.5 \times 5 \times 0 = \frac{0}{75}$$

E. AVERAGE ALL AREAS

$$\frac{10 + 50 + 10 + 5 + 0}{5} = 15$$

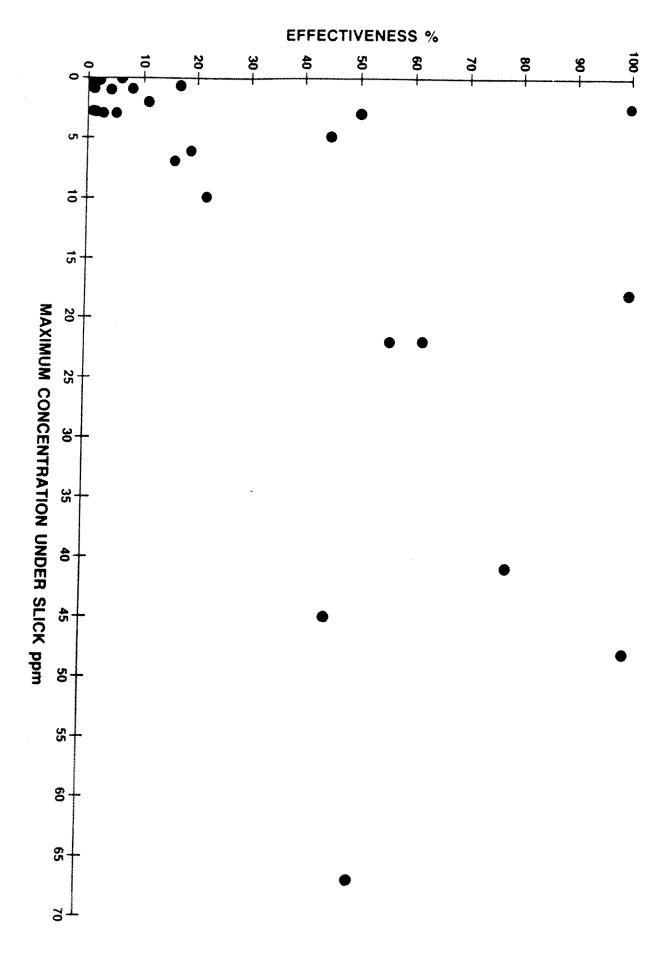
$$5 \times 5 \times 15 = 375$$

TABLE 3 -- Effectiveness estimators using maximum water column values alone  $^{1}$ 

			Effectiveness	Effectiveness
	Effectiveness <sup>2</sup>	Effectiveness	(%) if	(%) if
	(%) if equally	(%) if equally	distributed as	distributed as
Concentration in	distributed	distributed	a square function	a square function
ppm at 1 metre	to 1 metre	to 2 metres	to 2 metres	to 5 metres
1	1	2	3	5
2	2	4	6	9
5	5	10	14	23
10	10	20	29	45
20	20	40	57	91
30	30	60	86	•
50	50	100	-	-
75	75	-	<b>.</b>	-
100	100	-	-	-

<sup>1.</sup> The use of these estimates is not suggested as oil has been shown not to form a uniform downward plume. This table is presented here only as an example of this technique.

<sup>2.</sup> All examples assume a starting slick thickness of 100 microns.



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spatially oriented with the surface slick, that oil in the water column would not resurface, and that a simple integration scheme could accurately sum the amount of oil in the water column. This paper has shown that none of the assumptions are entirely true and that measurement of effectiveness using water column oil concentrations is not an accurate or reliable means. Recent measurements of oil remaining on the surface using remote sensing data are more accurate. However, they depend on the assumption that thickness of the slicks are identical. Tests of this type have been performed only on the short term and the accuracy of slick thickness measurements is poor.

There exist no empirical relationships between slick position, sub-surface plume concentrations, and time. Sub-surface concentration of oil 30 minutes after application of dispersant does, however, follow a square root or log function equally well. There appears to be no correlation between maximum sub-surface concentration and dispersant effectiveness.

Analytical means appear to be adequate for sub-surface concentration measurement, but are lacking for surface thickness measurements, and for dispersant in oil or in water measurements.

Experimenters have observed a number of phenomena during field trials. These include herding, re-surfacing of dispersed oil, and formation of emulsion particles. All of these interfere with the assessment or measurement of effectiveness. EFERENCES

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